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(54) Title: PRODUCTION OF COMPACTED BIOCIDAL AGENT FROM A NON-COMPACTIBLE PARTICULATE BIOCIDAL AGENT WITHOUT USING A BINDER

(57) Abstract: A shape-retentive compacted article is produced from 1,3-dibromo-5,5-dimethylhydantoin particulate solids by (a) granulating the particulate solids without use of a binder, and (b) pressure compacting granulated 1,3-dibromo-5,5-dimethylhydantoin granules formed in (a) that have a U.S. standard mesh size in the range of 80 mesh to 3 mesh, again without use of a binder. So far as is known, never before have 1,3-dibromo-5,5-dimethylhydantoin particulate solids been converted into a compacted form by any method.

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**PRODUCTION OF COMPACTED BIOCIDAL AGENT FROM A
NON-COMPACTIBLE PARTICULATE BIOCIDAL AGENT WITHOUT
USING A BINDER**

BACKGROUND

5 1,3-Dibromo-5,5-dimethylhydantoin has been produced commercially. The product, as produced and sold, is in the form of a fine powder. Its principal use is as source of bromine in conducting bromination reactions in chemical syntheses.

Widely used as a biocidal agent for water are N,N'-bromochloro-5,5-dialkylhydantoins. One of the features emphasized for such materials is that in use, the chlorine released from the biocide
10 regenerates active bromine from inactive bromide species formed during the water treatment operation. In other words, the chlorine atom in the initial N,N'-bromochloro-5,5-dialkylhydantoin is in effect regarded as a precursor for additional active bromine for sanitation purposes.

As is well known in the art, a deficiency of chlorine, of hypochlorites, and of certain halogenated organic water-treating agents is the formation during usage of undesirable disinfection
15 by-products. These by-products are undesirable both from the standpoint of environmental concerns and also from the standpoint of toxicological considerations.

Although 1,3-dibromo-5,5-dimethylhydantoin is referred to in patent disclosures as one of a group of biocidal agents for water treatment, so far as is known, this compound in its pure or concentrated state has never achieved commercial use as a biocide in water treatment. Instead, in
20 the prior art, only when in admixture with much larger quantities of N,N'-bromochloro-5,5-dimethylhydantoin was 1,3-dibromo-5,5-dimethylhydantoin deemed suitable for use in water sanitation.

SUMMARY OF THE INVENTION

This invention is based on several new discoveries. First of all, one of us and some of our
25 colleagues have discovered unexpectedly that 1,3-dibromo-5,5-dimethylhydantoin when used in treating water achieves the requirements of the U.S. Environmental Protection Agency at a dosage level that is only one-half of that required when using one or a mixture of N,N'-bromochloro-5,5-dialkylhydantoins. This discovery enables the use of extremely small concentrations of the 1,3-dibromo-5,5-dimethylhydantoin to effectively sanitize water while at the same time achieving

excellent microbiological control. Further, the ability to effectively utilize such small concentrations is expected to result in significant reduction in formation of disinfection by-products.

Moreover, it has also been discovered that 1,3-dibromo-5,5-dimethylhydantoin is also highly effective in combating biofilms which are microbiological slimes that form and prosper on surfaces in industrial and recreational water systems.

Such surprising and highly beneficial discoveries are more fully described in commonly-owned Application No.09/484,938.

This invention involves, in part, the discovery was that samples of commercially-produced 1,3-dibromo-5,5-dimethylhydantoin particulate solids obtained from three different commercial sources could not be pressure compacted into shape-retentive tablets without use of a binder. All attempts to produce tablets without use of a binder resulted in utter failure -- the compacted particles delaminated and broke into pieces during extraction from the die. Thus the commercially-produced 1,3-dibromo-5,5-dimethylhydantoin particulate solids could not be converted into tablets or briquettes, which are forms in which water treating biocides are commonly used, without first mixing the commercially-produced 1,3-dibromo-5,5-dimethylhydantoin particulate solids with a binding agent, commonly referred to as a binder.

Pursuant to this invention it has been further discovered, *inter alia*, that it is indeed possible to produce compacted forms of non-compactible 1,3-dibromo-5,5-dimethylhydantoin particulate solids without use of a binder. This can be accomplished by granulating non-compactible 1,3-dibromo-5,5-dimethylhydantoin particulate solids without use of a binder, and pressure compacting the granulated 1,3-dibromo-5,5-dimethylhydantoin, again without use of a binder.

Another embodiment of this invention is the provision of compacted articles such as granules, tablets, briquettes, and pucks produced, without use of a binder, using a process of this invention. In preferred forms, such articles have a crush strength of at least 6.81 kg per 2.54 cm (15 pounds per inch), and typically in the range of 6.81 to 31.8 kg per 2.54 cm (15 to 70 pounds per inch) of thickness.

These and other embodiments and features of this invention will be still further apparent from the ensuing description and appended claims.

FURTHER DETAILED DESCRIPTION OF THIS INVENTION

For ease of reference, the term "non-compactible" is used herein to denote that the given 1,3-dibromo-5,5-dimethylhydantoin particulate solids referred to cannot, without prior treatment to

enhance its compactibility, be successfully converted into a shape-retentive tablet when subjected to the following conditions:

- 1) A 1.80 cm- (0.71- inch) diameter circular die fabricated from Hastelloy® C alloy is lightly dusted with micronized polypropylene wax (MICROPRO 400 wax; Micro Powders, Incorporated, Tarrytown NY, or equivalent if MICROPRO 400 wax is not available).
- 2) A representative five-gram sample of the given 1,3-dibromo-5,5-dimethylhydantoin is manually placed into the above die.
- 3) The five-gram sample is pressure compacted in the die at 34,475 pKa (5000 psi) using a Sintech® press (MTS Systems Corporation, Edenprairie, Minnesota) equipped with a punch fabricated from Hastelloy® C alloy to form a 1.80 cm- (0.71-inch) diameter circular tablet. No dwell time is used, *i.e.*, the pressure is released just as soon as the pressure reaches 34,475 pKa (5000 psi).
- 4) If delamination or breakage occurs when the tablet is released from the die, the given 1,3-dibromo-5,5-dimethylhydantoin is deemed "non-compactible."

Conversely, the term "compactible" means that the 1,3-dibromo-5,5-dimethylhydantoin particulate solids referred to can be successfully converted into a shape-retentive tablet under the conditions just described in the immediately preceding paragraph.

This invention is applicable to both compactible and non-compactible 1,3-dibromo-5,5-dimethylhydantoin. However, generally speaking it is preferred to utilize this invention with non-compactible 1,3-dibromo-5,5-dimethylhydantoin, since so far as is known, there is no other way of pressure compacting non-compactible 1,3-dibromo-5,5-dimethylhydantoin into a shape-retentive article in a die without use of a binder.

A preferred process of this invention comprises the following steps:

- a) compressing compactible or, preferably, non-compactible 1,3-dibromo-5,5-dimethylhydantoin particulate solids in the absence of a binder into a sheet of a thickness in the range of 0.16 cm and 1.27 cm (1/16 inch and 1/2 inch);
- b) subdividing such sheet into particles comprising particles in the range of 80 mesh to 3 U.S. standard mesh size, and preferably in the range of 30 mesh to 8 U.S. standard mesh size;
- c) pressure compacting particles from b) in the range of 80 mesh to 3 U.S. standard mesh size, preferably particles in the range of 30 mesh to 8 U.S. standard mesh size, in a die in the absence of a binder mixed therewith.

Compression in a) can be conducted in any suitable press capable of applying suitable compression pressure, which typically is in the range of 6,895 kPa to 206,850 kPa (1000 to 30,000 psi), and

preferably in the range of 34,475 kPa to 172,375 kPa (5000 to 25,000 psi). Preferred apparatus for such compression is a set of compression rolls. The resultant compressed shape, typically in the form of a sheet or other suitable breakable form, is then broken up into small granules in a suitable apparatus, such as, for example, in a Chilsonator[®] breaker (The Fitzpatrick Company, Elmhurst, Illinois). The particles in the size ranges referred to in b) are regarded as granulated 1,3-dibromo-5,5-dimethylhydantoin. If in b) particles are also formed that are larger and/or smaller than the selected size referred to in b), it is preferred to classify the particles formed in b) into (1) a fraction containing the particles in the selected size range of b), and (2) either or both of (i) a fraction composed of the larger particles, and/or (ii) a fraction composed of the smaller particles, as the case may be. Where a fraction of (i) exists, such fraction is preferably recycled to b). Where a fraction of (ii) exists, such fraction is preferably recycled to a).

If desired, the surfaces of the die used in c) may be lubricated with a suitable lubricant to facilitate removal of the compacted article from the die. However, as noted, no binder is used in this operation or for that matter, none is used in step a) either.

The time period during which the pressure is applied to the 1,3-dibromo-5,5-dimethylhydantoin solids in a) and in c) is not critical. As long as suitable compaction is achieved, the time of compaction is of little or no consequence. In any situation where the optimum time has not been previously determined, a few simple preliminary tests should readily enable such pressure conditions, including pressure times, to be determined and optimized.

The compaction or compression steps in a) and c) above are typically initiated with the 1,3-dibromo-5,5-dimethylhydantoin solids at room temperature. However, if desired, the solids can be preheated or precooled such that the compaction or compression is initiated at a temperature in the range of 5 to 80°C.

If desired, the 1,3-dibromo-5,5-dimethylhydantoin particulate solids can be formulated with suitable excipients such as disintegrants, lubricants, and mold release agents. Other optional ingredients which may be used in the formulation of products from the 1,3-dibromo-5,5-dimethylhydantoin particulate solids include fragrances, stabilizers, corrosion inhibitors, dyes, other biocidal agents, surfactants, effervescent, diluents, builders, and chelating agents. Such ancillary materials should of course be compatible with 1,3-dibromo-5,5-dimethylhydantoin and not interfere in any material way with the excellent performance characteristics of the 1,3-dibromo-5,5-dimethylhydantoin particulate solids of this invention. The amount(s) of such ancillary materials used should of course be sufficient to serve the purpose for which it is, or they are, being used. At

the same time, the amount used should not materially detract from the physical, mechanical, or performance properties of the formulated product.

Example 1 illustrates background discoveries dealt with more fully in commonly-owned copending Application No. 09/484,891. One such discovery is that 1,3-dichloro-5,5-dimethylhydantoin and N,N'-bromochloro-5,5-dimethylhydantoin particulate solids can be pressure compacted into shape-retentive tablets without use of a binder. Another such discovery is that samples of commercially-available 1,3-dibromo-5,5-dimethylhydantoin obtained from three different producers could not be pressure compacted into shape-retentive tablets without use of a binder.

EXAMPLE 1

Five-gram samples of 1,3-dibromo-5,5-dimethylhydantoin products obtained from three separate commercial sources were compacted without binder in a Sintech® press (MTS Systems Corporation, Edenprairie, Minnesota) equipped with a punch and die fabricated from Hastelloy® C alloy. Before compaction the interior of the tooling surfaces were lightly dusted with a micronized wax to facilitate release of tablets from the mold. The pressure applied was 34,475 kPa (5000 psi) with no dwell time. Three samples of each commercial product were subjected to these compression tests. For comparison, four-gram samples of 1,3-dichloro-5,5-dimethylhydantoin and of N,N'-bromochloro-5,5-dimethylhydantoin as received were tested in the same manner without use of a binder. It was found that shape-retentive tablets of 1,3-dibromo-5,5-dimethylhydantoin could not be produced under these conditions, whereas the two other 1,3-dihalo-5,5-dimethylhydantoin products were successfully tableted under the same conditions. The tablets formed from the 1,3-dichloro-5,5-dimethylhydantoin and from the N,N'-bromochloro-5,5-dimethylhydantoin after removal from the die were aged for 6 days at room temperature. Thereupon the tablets were subjected to crush strength testing utilizing a Sintech® 1/S compression apparatus (MTS Systems Corporation, Edenprairie, Minnesota) equipped with Testworks software, which software is installed in the 1/S compression apparatus as supplied by MTS Systems Corporation. The apparatus includes a horizontal circular-shaped load cell interfaced with a computer, a digital micrometer also interfaced with the computer, and a vertical screw-driven piston that is disposed above the load cell and adapted to apply a downward force perpendicular to the load cell. The procedure for measuring crush strength involves measuring the thickness of the tablet with the micrometer to provide a digitized input to the computer. Next the tablet is placed on its edge on the load cell with the piston in contact with the upper edge of the tablet. Then the apparatus is activated whereby the piston commences

applying a progressively increasing downward diametral force to the tablet. At the same time, the load cell continuously measures the downward force being applied to the tablet, and the input of such measurements is transmitted to the computer. When the force being applied reaches the point where the amount of force suddenly decreases to 10% of the immediately preceding force, the tablet has reached the breaking point, and the application of the force is immediately terminated by the software program. From the inputs to the computer, two values are provided, namely the pounds of force at the breaking point of the tablet, and the pounds of force per inch thickness of the tablet at the breaking point. Thus the greater the force applied, the greater the crush strength. Table 1 lists the average particle sizes and particle size distributions of the five commercial products as received. In those cases where it was possible to form a tablet, Table 1 also provides the results of the crush strength tests on such tablets. For convenience, the following abbreviations are used in Table 1: DBDMH is 1,3-dibromo-5,5-dimethylhydantoin, DCDMH is 1,3-dichloro-5,5-dimethylhydantoin, and BCDMH is N,N'-bromochloro-5,5-dimethylhydantoin.

TABLE 1

Particle Size	DCDMH - Aldrich	BCDMH - Aldrich	DBDMH - Aldrich	DBDMH - Albemarle	DBDMH - Great Lakes
Average	108.1 μ	323.8 μ	162.1 μ	64.59 μ	45.23 μ
10% is greater than	195.3 μ	877.9 μ	359.2 μ	162.7 μ	78.76 μ
25% is greater than	134.4 μ	409.9 μ	177.6 μ	90.12 μ	49.76 μ
50% is greater than	80.07 μ	173.9 μ	86.03 μ	39.21 μ	34.68 μ
75% is greater than	45.99 μ	65.39 μ	47.37 μ	26.85 μ	23.25 μ
90% is greater than	27.19 μ	29.35 μ	27.67 μ	17.91 μ	13.90 μ
Range	0.04 - >2000 μ	0.04 - >2000 μ	0.04 - >2000 μ	0.04-309.6 μ	0.04-409.6 μ
Compaction	Intact tablets	Intact tablets	Delaminated; broken tablets	Delaminated; broken tablets	Delaminated; broken tablets
Crush strength lb/in	183.6	83.9	Test not possible	Test not possible	Test not possible

It can be seen from Example 1 that the compaction characteristics of the prior commercially-available 1,3-dibromo-5,5-dimethylhydantoin are vastly different from the compaction characteristics of the prior commercially-available 1,3-dichloro-5,5-dimethylhydantoin and N,N'-dichloro-5,5-dimethylhydantoin.

Example 2 illustrates the discovery, pursuant to this invention, that despite its vastly different compaction characteristics, 1,3-dibromo-5,5-dimethylhydantoin particulate solids of the type that are not amenable to successful one-step pressure compaction into shape-retentive articles such as tablets without use of a binder, can be converted into shape-retentive articles such as tablets without use of a binder if a compaction process pursuant to this invention is used.

EXAMPLE 2

A sample of commercially-produced 1,3-dibromo-5,5-dimethylhydantoin (Albemarle Corporation), having an average particle size of about 64.5μ , is compressed into sheet form in a continuous fashion by means of a proprietary MS-75 compactor system (Hosokawa Bepex, Minneapolis, Minnesota). Five-gram samples of 1,3-dibromo-5,5-dimethylhydantoin in the range of 8 to 30 mesh size are compacted without binder in a Sintech[®] press (MTS Systems Corporation, Edenprairie, Minnesota) equipped with a punch and die fabricated from Hastelloy[®] C alloy. Before manually filling the die, the interior surfaces of the die are lightly dusted with a micronized polypropylene wax (MICROPRO 400 wax; Micro Powders, Incorporated, Tarrytown, NY). The pressure applied is 34,475 kPa (5000 psi) with no dwell time, *i.e.*, the pressure is released as soon as the increasing pressure reaches 34,475 kPa (5000 psi). In an operation conducted in this general manner, intact tablets with the appearance of some friability at the ridges were obtained. The tablets were aged for 6 days at room temperature. Thereupon the tablets were subjected to crush strength testing utilizing the apparatus and procedure for crush strength measurements as described in Example 1 above. In duplicate determinations, the tablets were found to have an average crush strength in the diametral direction averaging 12.7 kg per 2.54 cm (28 pounds per inch).

As used herein, including the claims, values given for crush strength are as measured using the apparatus and procedure as described in Example 1 above. When the compacted article is in a form other than a cylindrical tablet, the article being tested is to be positioned on the load cell and under the screw-driven piston with the longest axis of the article in the vertical position. In addition, the micrometer is used to measure the thickest portion of the article when the article is positioned on the load cell and under the screw-driven piston with the longest axis of the article in the vertical position.

Compounds referred to by chemical name or formula anywhere in this document, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (*e.g.*, another component, or a solvent). It matters not what preliminary chemical changes, if any, take place in the resulting mixture

or solution, as such changes are the natural result of bringing the specified substances together under the conditions called for pursuant to this disclosure. Also, even though the claims may refer to substances in the present tense (*e.g.*, "comprises," "is"), the reference is to the substance as it exists at the time just before it is first contacted, blended or mixed with one or more other substances in accordance with the present disclosure.

Except as may be expressly otherwise indicated, the article "a" or "an" if and as used herein is not intended to limit, and should not be construed as limiting, a claim to a single element to which the article refers. Rather, the article "a" or "an" if and as used herein is intended to cover one or more such elements, unless the text expressly indicates otherwise.

This invention is susceptible to considerable variation in its practice. Therefore the foregoing description is not intended to limit, and should not be construed as limiting, the invention to the particular exemplifications presented hereinabove. Rather, what is intended to be covered is as set forth in the ensuing claims and the equivalents thereof permitted as a matter of law.

THAT WHICH IS CLAIMED IS:

1. A method of producing a shape-retentive compacted article from 1,3-dibromo-5,5-dimethylhydantoin particulate solids, which method comprises:

- 5 a) granulating 1,3-dibromo-5,5-dimethylhydantoin particulate solids without use of a binder, and
- b) pressure compacting granulated 1,3-dibromo-5,5-dimethylhydantoin granules formed in a) that have a U.S. standard mesh size in the range of 80 mesh to 3 mesh, again without use of a binder.

10 2. A method of Claim 1 wherein said 1,3-dibromo-5,5-dimethylhydantoin particulate solids used in a) cannot be successfully converted without granulation as in a) into a shape-retentive tablet that does not delaminate or break when released from the die in a procedure in which a five-gram sample of such solids is manually placed into a die of Hastelloy® C alloy that has been lightly dusted with micronized polypropylene wax, and is pressure compacted in the die at 34,475 kPa (5000 psi) into a 1.80 cm- (0.71-inch) diameter circular tablet, with no dwell time.

15 3. A method of producing a shape-retentive compacted article from 1,3-dibromo-5,5-dimethylhydantoin particulate solids, which method comprises:

- a) compressing 1,3-dibromo-5,5-dimethylhydantoin particulate solids in the absence of a binder into a sheet of a thickness in the range of 0.16 cm to 1.27 cm (1/16 inch to 1/2 inch);
- 20 b) subdividing such sheet into particles comprising particles in the range of 80 mesh to 3 U.S. standard mesh size; and
- c) pressure compacting particles from b) in the range of 80 mesh to 3 U.S. standard mesh size in a die in the absence of a binder mixed therewith.

4. A method of Claim 3 wherein said particles in b) and in c) are in the range of 30 mesh to 8 U.S. standard mesh size.

25 5. A method of Claim 3 or 4 wherein the compression in a) is conducted with the application of compression pressure in the range of 6.895 to 206,850 kPa (1000 to 30,000 psi).

6. A method of Claim 3 or 4 wherein the compression in a) is conducted with the application of compression pressure in a set of compression rolls in the range of 34,475 to 172,375 kPa (5000 to 25,000 psi).

30 7. A method of Claim 3 or 4 wherein the particles formed in b) are classified into (1) a fraction containing the particles in the size range of b), and (2) either or both of (i) a fraction

composed of the larger particles, and/or (ii) a fraction composed of the smaller particles, as the case may be.

8. A method of Claim 7 where a fraction of (i) if it exists, is recycled to b), and a fraction of (ii) if it exists, is recycled to a).

5 9. A pressure compacted article of 1,3-dibromo-5,5-dimethylhydantoin produced by a method comprising:

a) granulating 1,3-dibromo-5,5-dimethylhydantoin particulate solids without use of a binder, and

10 b) pressure compacting granulated 1,3-dibromo-5,5-dimethylhydantoin granules formed in a) that have a U.S. standard mesh size in the range of 80 mesh to 3 mesh, again without use of a binder.

10. A pressure compacted article of 1,3-dibromo-5,5-dimethylhydantoin by a method comprising:

15 a) compressing 1,3-dibromo-5,5-dimethylhydantoin particulate solids in the absence of a binder into a sheet of a thickness in the range of 0.16 cm to 1.27 cm (1/16 inch to 1/2 inch);

b) subdividing such sheet into particles comprising particles in the range of 80 mesh to 3 U.S. standard mesh size; and

c) pressure compacting particles from b) in the range of 80 mesh to 3 U.S. standard mesh size in a die in the absence of a binder mixed therewith.

20 11. An article of Claim 10 wherein said particles in b) and in c) are in the range of 30 mesh to 8 U.S. standard mesh size.

12. An article of Claim 10 wherein the compression in a) is conducted with the application of compression pressure in the range of 6,895 to 206,850 kPa (1000 to 30,000 psi).

25 13. An article of Claim 10 wherein the compression in a) is conducted with the application of compression pressure in a set of compression rolls in the range of 34,475 to 172,375 kPa (5000 to about 25,000 psi).

14. A pressure compacted article of any of Claims 9-13 inclusive, having a crush strength in the range of 6.8 to 31.8 kg per 2.54 cm (15 to 70 pounds per inch) of thickness.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 01/01541

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C02F1/50 A01N43/50 A01N43/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C02F A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	WO 97 15652 A (MAINQUIST WILLIAM K ;CLOROX CO (US); RADER JAMES E (US)) 1 May 1997 (1997-05-01) page 6, line 4 -page 8, line 5	1,2,9-11 3-8, 12-14
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *8* document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

PCT/US 01/01541

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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